Antunes Staffolani

Via Monsignor Francesco Liverani 59,
Ravenna (RA), 48121
+39 3341749533
antunes.staffolani@gmail.com
antunes.staffolani@unibo.it
https://www.linkedin.com/in/antunes-staffolani-16b7b8118/

22/12/1993

Ph.D. Antunes Staffolani is a Junior Researcher in Inorganic Chemistry (RTDa in CHIM/03) funded by PNRR CN-MOST spoke 13 (Sustainable Mobility Center, NextGeneration EU) at the Department of Chemistry "Giacomo Ciamician" of the University of Bologna. He is also affiliated with the Interdepartmental Industrial Research Center for Renewable Sources, Environment, Sea, and Energy of the University of Bologna (CIRI-FRAME). His research activity is performed at the Enercube lab - technology transfer laboratory of electrochemical systems. His expertise ranges from (i) development and characterization of active materials for next-generation Li-ion and Na-ion batteries, with a particular focus on anode materials, and (ii) novel electrochemical techniques and their implementation, with a focus on electrochemical impedance spectroscopy and its related data elaboration. Furthermore, his experience also includes the study of recycling methodologies for Li-ion batteries via green soft-hydrometallurgy, and/or direct recycling. He is author and co-author of 14 research papers on peer-reviewed scientific journals, with a h-index of 8 and 1 patent.

Experience

MAY 2023 – PRESENT

Junior Assistant Professor (RTDa funded by PNRR CN-MOST spoke 13)

University of Bologna, Department of Chemistry "Giacomo Ciamician" and CIRI-FRAME

Supervisor: Prof. Francesca Soavi

Duration: 3-year contract

Research contract funded by the PNRR action under the project CN-MOST (Sustainable Mobility Center). The research work is focused on the development of novel, high performance, and sustainable materials for electrochemical energy storage and conversion devices such as Li-ion batteries, post-Li devices (Li-air, Na-ion etc.), supercapacitors, and PEM-fuel cells. Furthermore, the work is also centred on recycling and design for recycling of Li-ion batteries. Furthermore, one of the main tasks is the technology transfer of the project results through collaborations with industrial partners. Moreover, he is Course Lecturer for the course "General and Inorganic Chemistry" for the faculty of Conservation and Restoration of Cultural Heritage (6 ECTS - 56 h course, Ravenna campus).

APRIL 2022 – MAY 2023

Post-doctoral researcher

University of Camerino, School of Science and Technology, Chemistry division.

Supervisor: Prof. Francesco Nobili

Duration: 1-year contract

The research work was focused on the development of anode and cathode materials for Na-ion batteries based on Sn and Prussian Blue Analogues, respectively. Furthermore, electrochemical characterization of commercial-size solid oxide fuel cells by electrochemical impedance spectroscopy was pursued in collaboration with the University of Perugia (Prof. Linda Barelli's group). Moreover, the study of recycling routes based on soft-hydrometallurgy and direct recycling was done in collaboration with Midac S.p.A.

30TH OF NOVEMBER 2018 – 4TH OF APRIL 2022

Ph.D. in Chemical Sciences

University of Camerino, School of Science and Technology, Chemistry division.

Supervisor: Prof. Francesco Nobili

Title of the thesis: Investigation of Interfacial and Transport properties of LIBs/NIBs anodes and commercial SOFCs

Thesis reviewers: Prof. Maria Assunta Navarra (Sapienza University of Rome)
Prof. Claudio Gerbaldi (Polytechnic University of Turin)

Examination commissioner: Prof. Teofilo Rojo (Universidad de Pais Vasco)

Final mark: Excellent

Ph.D. funded by University of Camerino and Prof. Francesco Nobili's group. The objective of the Ph.D. was the development of anode materials for both Li- and Na-ion batteries based on the conversion-alloying mechanism. Furthermore, the thesis work also includes the electrochemical characterization of lab-scale solid oxide fuel cells by electrochemical impedance spectroscopy and its deconvolution given by the calculation of the distribution (function) of relaxation times (work done in collaboration with Prof. Linda Barelli's group).

Several works were formally not included in the Ph.D. thesis for consistency reasons and include: (i) development of protective coatings against Cr-poisoning in SOFCs, (ii) recycling of Li-ion batteries soft-hydrometallurgy and direct recycling (collaboration with Midac S.p.A.).

JANUARY 2018 – OCTOBER 2018

R&D Chemist

Orim S.p.A., Piediripa di Macerata (MC).

Work contract as R&D chemist at the company Orim S.p.A. located in Piediripa di Macerata (MC). The work was focused on the research and development at pre-industrial scale of hydrometallurgical methods for the recovery and recycling of valuable non-ferrous metals from industrial waste such as: spent catalysts based on Ni, Co, V, Mn, Mo etc…, and precious metals given by waste from Electrical and Electronic Equipment (WEEE).

Education

4TH OF DECEMBER 2017

M.sc. Degree in "Quimica"

Instituto Superior Técnico of Lisbon, Lisbon, Portugal

Supervisors:	Prof. Maria de Fátima Grilo da Costa Montemor
	Prof. Francesco Nobili
Title of the thesis:	Iron-Oxide based anodes for Li-ion Batteries: Synthesis and Characterization
Final mark:	18/20

Msc. Thesis work based on the development and characterization of anode materials for Li-ion batteries based on Fe_3O_4 and Fe_2O_3. In this work, three different anode materials were synthesized, i.e., bare Fe_3O_4 nanoparticles, Fe_3O_4 composite with reduced graphene oxide, and nanostructured Fe_2O_3 by a vanillin-assisted synthesis. The materials were then characterized by several techniques, which includes scanning electron microscopy, X-Ray Diffraction, thermogravimetric analysis, galvanostatic cycling, cyclic voltammetry, rate capability, and electrochemical impedance spectroscopy.

Exams taken during the period abroad	Industrial Chemistry (6 ECTS).
	Pharmaceutical Chemistry (6 ECTS).
	Medicinal Chemistry (6 ECTS).
	Photochemical Processes (6 ECTS).
	Specialization Laboratory I (6 ECTS).

12TH OF OCTOBER 2017

M.sc. Degree in "Chemistry and Advanced Chemical Methodology"

Università di Camerino, School of Science and Technology, Chemistry division

Supervisors: Prof. Francesco Nobili

Title of the thesis: Iron-Oxide based anodes for Li-ion Batteries: Synthesis and Characterization

Final mark: 110 cum laude/110

Msc. Thesis work based on the development and characterization of anode materials for Li-ion batteries based on Fe_3O_4 and Fe_2O_3. In this work, three different anode materials were synthesized, i.e., bare Fe_3O_4 nanoparticles, Fe_3O_4 composite with reduced graphene oxide, and nanostructured Fe_2O_3 by a vanillin-assisted synthesis. The materials were then characterized by several techniques, which includes scanning electron microscopy, X-Ray Diffraction, thermogravimetric analysis, galvanostatic cycling, cyclic voltammetry, rate capability, and electrochemical impedance spectroscopy.

15TH OF OCTOBER 2015

B.sc. Degree in "Chemistry and Advanced Chemical Methodology"

Università di Camerino, School of Science and Technology, Chemistry division

Supervisors: Prof. Francesco Nobili

Title of the thesis: **Caratterizzazione Elettrochimica di Elettrodi Green a base di $Li_4Ti_5O_{12}$**

Final mark: 110 cum laude/110

B.sc. thesis work based on the production of green electrodes based on the anode material $Li_4Ti_5O_{12}$ (LTO). Three different anode materials were tested, i.e., bare LTO nanoparticles, heat-treated LTO, and carbon coated LTO. The materials were characterized by X-Ray Diffraction while the electrodes were characterized by galvanostatic cycling, cyclic voltammetry, rate capability.

Bibliographic data

	Scopus	Web of Science	Google scholar	ResearchGate
Papers	14	14	14	14
Citations	155	139	195	168
h-index	8	8	8	8

Awards

- IWES 2021 lecturer award for the presentation “Fast Charging Anode for LIBs and NIBs Based on Fe_3O_4/rGO: Synthesis and Characterization”.
- Grant for the participation to the conference “Enerchem 2” held in Padova 12-14/02/2020.

Projects participation

MISE – ENEA 2019-2024

Ricerca di sistema elettrico - Sistemi di accumulo e relative interfacce con le reti – accumulo elettrochimico 2019-2021

Synthesis and characterization of novel anode materials for both Li-ion and Na-ion batteries. Study of the electrode/electrolyte interface.

Ricerca di sistema elettrico - Sistemi di accumulo e relative interfacce con le reti – accumulo elettrochimico 2022-2024

Studi di sintesi e caratterizzazione di catodi a base di analoghi blu di Prussia.

PNRR MOST 2023-2026

PNRR spoke 13 CN-MOST (National Sustainable Mobility Center)

Development of materials and production and recovery processes of current and next-generation electrochemical energy storage/conversion cells of improved performance and sustainability. Development of high-power cells through three main strategies, which will be conducted with attention to the sustainability of materials and processes: a) development of lithium and post-lithium cell materials operating at high C-rates (electrodes, separators, electrolytes, stable at high operating temperatures typical of power applications), b) development of alternative electrode materials characterized by high process kinetics (including capacitive systems such as lithium-ion capacitors, hybrid supercapacitors) and their integration, c) analysis and diagnosis (ex-situ, in-situ and in-operando) of materials and cells under high power operation using advanced techniques. Technology transfer of the project results through collaborations with industrial partners and/or spin-offs.

Cross-sectoral solutions for the climate transition (HORIZON-CL5-2021-D2-01) - 2021

Participation as partner (without my Ph.D. supervisor) on the Horizon call CL5-2021-D2-01 "Cross-sectoral solutions for the climate transition". The proposed project, called Be-CYCLIC, focused on the production of Gen3b Li-ion batteries and, especially, their recycling via soft-hydrometallurgy and direct recycling. Unfortunately, it was not funded.

Mobility project with the Ecole Polytechnique de Montréal for teaching and research activities

Principal investigator of a mobility project with the Ecole Polytechnique de Montréal for teaching and research activities. The project deals with lecture and laboratory activities about the "electrochemistry of the processes occurring at the electrodes interface". Furthermore, research activities in the topic of "ion-gated transistors" were carried out in collaboration with Prof. Clara Santato.

Reviewer activities

- Materials (Mdpi).
- Applied Sciences (Mdpi).
- Batteries (Mdpi).
- Materials Research Bulletin (Elsevier).
- Advanced Engineering Materials (Wiley-CH).

Third mission activities

Midac S.p.A.

Civitanova Marche (MC) – Soave (VR)

30/07/2021-26/10/2021, 100 h

Type: Consultancy contract

Assistance in writing a Horizon Europe project proposal.

Assistance in designing a new electrochemical laboratory for the company.

Comas S.p.A.

Bologna (BO)

05/05/2023 - Now

Type: Co-supervisor of the Ph.D. student Shoayb Mojtahedi

Assistance in the research work of the Ph.D. student and exchange of knowledge with the company.

Research focused on dry electrode preparation for Lithium-ion batteries.

Ferrari S.p.A.

Bologna (BO)

05/05/2023 - Now

Type: Co-supervisor of the Ph.D. student Alessandro Gregucci

Assistance in the research work of the Ph.D. student and exchange of knowledge with the company. Research focused on Li-ion Cell Internal Design, Monitoring & Diagnosis.

Ricircola – Reale mutua assicurazioni

Ravenna (RA)

04/10/2023 – 2 h

Type: Consultancy contract

2 h lecture on working principles, safety, and hazards of Li-ion batteries.

Ripensaci – Notte dei ricercatori

Centro di ricerca Ambiente, Energia, e Mare – Marina di Ravenna (RA)

29/09/2023

Teaching activities

University of Bologna – Electrochemical devices for the environment and energy

Environmental sciences (L 32)

Type: Exam commissioner

University of Bologna – General and inorganic chemistry and laboratory

Environmental sciences (L 32)

Type: Exam commissioner

University of Bologna – Electrochemical energy storage and conversion

Electric vehicle engineering (LM 28)

Electrical energy engineering (LM 28)

Advanced automotive engineering (LM 33)

Type: Exam commissioner

University of Bologna - General and inorganic chemistry and laboratory

Conservation and Restoration of Cultural Heritage (LMR/02)

25/09/2023-12/11/2023, 56 h course (6 ECTS)

Type: Course lecturer (laboratory & lessons)

University of Camerino - Laboratory of physical chemistry I

B.Sc. in Chemical Sciences (L 27)

12/01/2021 – 28/01/2021, 27 h course

Type: Teaching tutor (laboratory)

University of Camerino - Laboratory of analytical chemistry II

B.Sc. in Chemical Sciences (L 27)

07/01/2019 – 15/01/2018, 40 h course

Type: Teaching tutor (laboratory)

University of Camerino - Laboratory of analytical chemistry II

B.Sc. in Chemical Sciences (L 27)

04/12/2017 – 12/12/2017, 42 h course

Type: Teaching tutor (laboratory)

University of Bologna - General and inorganic chemistry

B.Sc. in Nutrition Biology (L 13)

14/11/2017 – 20/12/2017, 14 h course

Type: Teaching tutor (lessons)

Thesis supervision

Co-supervisor of:

- 4 bachelor students' theses.
    - Claudio Magini – Disciplinary sector (CHIM/02 Physical chemistry) – L 27 Chemical Sciences – University of Camerino
    - Francesco Pirisi – Disciplinary sector (CHIM/02 Physical chemistry) – L 27 Chemical Sciences – University of Camerino
    - Francesca Stella – Disciplinary sector (CHIM/02 Physical chemistry) – L 27 Chemical Sciences – University of Camerino
    - Marzia Marchegiani – Disciplinary sector (CHIM/02 Physical chemistry) – L 27 Chemical Sciences – University of Camerino

- 7 master students' theses.
    - Leonardo Sbrascini – Disciplinary sector (CHIM/02 Physical chemistry) – LM 54 Chemistry and Advanced Chemical Methodologies – University of Camerino
    - Federico Verdicchio – Disciplinary sector (CHIM/02 Physical chemistry) – LM 54 Chemical Sciences – University of Perugia
    - Issah Musah– Disciplinary sector (CHIM/02 Physical chemistry) – LM 54 Chemistry and Advanced Chemical Methodologies – University of Camerino
    - Humar DIlixiati – Disciplinary sector (CHIM/02 Physical chemistry) – LM 54 Chemistry and Advanced Chemical Methodologies – University of Camerino
    - Andrea Trebbi – Disciplinary sector (CHIM/03 Inorganic chemistry) – LM 30 Energetic Engineering – University of Bologna
    - Aishabibi Ashir – Disciplinary sector (CHIM/03 Inorganic chemistry) – LM 35 Environmental and Terriotory engineering – University of Bologna
    - Edoardo Finaurini – Disciplinary sector (CHIM/02 Physical chemistry) – LM 54 Chemistry and Advanced Chemical Methodologies – University of Camerino

- 3 Ph.D. students' theses.
  - Alessandro Gregucci "Li-ion Cell Internal Design, Monitoring & Diagnosis" (co-funded by Ferrari S.p.A.) – Disciplinary sector (CHIM/03 Inorganic chemistry) – University of Bologna
  - Shoayb Mojtahedi "Dry electrodes preparation for Li-ion batteries" (co-funded by Comas S.p.A.) – Disciplinary sector (CHIM/03 Inorganic chemistry) – University of Bologna
  - Federico Mascetti "Recycling Li-ion batteries" (co-funded by Comas S.p.A.) – Disciplinary sector (CHIM/03 Inorganic chemistry) – University of Bologna

Supervisor of:

- 1 Master students' theses.
  - Jordi Falguera Garcia (CHIM/02 Physical chemistry) – Erasmus Mundus Master Degree in "Chemistry Innovation and Regulation" – University of Bologna

Active membership

- Member of the Italian Society of Chemistry – Electrochemistry division
- Member of the International Society of Electrochemistry

CHAPTER 2 – LIST OF PUBLICATIONS AND PATENTS

PEER-REVIEWED PUBLICATIONS

1) Carbonari, Gilberto; Maroni, Fabio; Gabrielli, Serena; **Staffolani, Antunes**; Tossici, Roberto; Palmieri, Alessandro; Nobili, Francesco. "Synthesis and characterization of vanillin-templated Fe_2O_3 nanoparticles as a sustainable anode material for Li-ion batteries". *ChemElectroChem* Vol. 6 (2019), no. 6, pp. 1915-1920. https://doi.org/10.1002/celc.201900189

2) Darjazi, Hamideh; **Staffolani, Antunes**; Sbrascini Leonardo; Bottoni, Luca; Tossici, Roberto; Nobili, Francesco. "Sustainable anodes for lithium- and sodium-ion batteries based on coffee ground-derived hard carbon and green binders". *Energies* Vol. 13 (2020), No. 23, pp. 6216. https://doi.org/10.3390/en13236216

3) Baldinelli, Arianna; **Staffolani, Antunes**; Bidini, Gianni; Barelli, Linda; Nobili, Francesco. "An extensive model for renewable energy electrochemical storage with Solid Oxide Cells based on a comprehensive analysis of impedance deconvolution" *Journal of Energy Storage* Vol. 33 (2021), pp. 102052. https://doi.org/10.1016/j.est.2020.102052 **Thesis related.**

4) **Staffolani, Antunes**; Baldinelli, Arianna; Barelli, Linda; Bidini, Gianni; Nobili, Francesco. "Early-stage detection of solid oxide cells anode degradation by operando impedance analysis" *Processes* Vol. 9 (2021), No. 5, pp.848. https://doi.org/10.3390/pr9050848 **Thesis related.**

5) **Staffolani, Antunes**; Darjazi, Hamideh; Carbonari, Gilberto; Maroni, Fabio; Gabrielli, Serena; Nobili, Francesco. "Fe_3O_4/graphene composite anode material for fast-charging li-ion batteries" *Molecules* Vol. 26 (2021), No. 14, pp. 4316. https://doi.org/10.3390/molecules26144316 **Thesis related.**

6) Sbrascini, Leonardo; **Staffolani, Antunes**; Bottoni, Luca; Darjazi, Hamideh; Minnetti, Luca; Minicucci, Marco; Nobili, Francesco. "Structural and Interfacial Characterization of a Sustainable Si/Hard Carbon Composite Anode for Lithium-Ion Batteries" *ACS Applied Materials & Interfaces* Vol. 14 (2022), No. 29, pp. 33257–33273. https://doi.org/10.1021/acsami.2c07888

7) **Staffolani, Antunes**; Baldinelli, Arianna; Bidini, Gianni; Nobili, Francesco; Barelli, Linda. "Operando Analysis of Losses in Commercial-Sized Solid Oxide Cells: Methodology Development and Validation" *Energies* Vol. 15 (2022), No. 14, pp. 4978. https://doi.org/10.3390/en15144978

8) Bottoni, Luca; Darjazi, Hamideh; Sbrascini, Leonardo; **Staffolani, Antunes**; Gabrielli, Serena; Pastore, Genny, Pastore; Tombesi, Alessia; Nobili, Francesco. "Electrochemical Characterization of Charge Storage at Anodes for

Sodium-Ion Batteries Based on Corncob Waste-Derived Hard Carbon and Binder” *ChemElectroChem* Vol. 10 (2023), No. 8, pp. e202201117. https://doi.org/10.1002/celc.202201117

9) Darjazi, Hamideh; Bottoni, Luca; Moazami, Hamid Reza; Rezvani, Seyed Javad; Balducci, Leonardo; Sbrascini, Leonardo; **Staffolani, Antunes**; Tombesi, Alessia; Nobili, Francesco. “From waste to resources: transforming olive leaves to hard carbon as sustainable and versatile electrode material for Li/Na-ion batteries and supercapacitors” *Materials Today Sustainability* Vol. 21 (2023), pp. 100313. https://doi.org/10.1016/j.mtsust.2022.100313

10) Minnetti, Luca; Marangon, Vittorio; Andreotti, Paolo; **Staffolani, Antunes**; Nobili, Francesco; Hassoun, Jusef. “Reciprocal irreversibility compensation of $LiNi_{0.2}Co_{0.2}Al_{0.1}Mn_{0.45}O_2$ cathode and silicon oxide anode in new Li-ion battery”. *Electrochimica Acta* Vol. 452 (2023), pp. 142263. https://doi.org/10.1016/j.electacta.2023.142263

11) Baldinelli, Arianna; **Staffolani, Antunes**; Nobili, Francesco; Barelli, Linda. “Detailed experimental analysis of solid oxide cells degradation due to frequent fuel cell/electrolyser switch”. *Journal of Energy Storage* Vol. 73, part C, pp. 109117. https://doi.org/10.1016/j.est.2023.109117

12) Marchese, Daniele; Giosuè, Chiara; **Staffolani, Antunes**; Conti, Massimo; Orcioni, Simone; Soavi, Francesca; Cavalletti, Matteo; Stipa, Pierluigi. “An Overview of the Sustainable Recycling Processes Used for Lithium-Ion Batteries”. *Batteries* Vol. 10 (2024), Issue 1. https://doi.org/10.3390/batteries10010027

13) Minnetti, Luca; Sbrascini, Leonardo; **Staffolani, Antunes**; Marangon, Vittorio; Nobili, Francesco; Hassoun, Jusef. “Unravelling the Ion Transport and the Interphase Properties of a Mixed Olivine Cathode for Na-ion Battery”. *Journal of Energy Chemistry* Vol.96 (2024), pp.300-317.

14) **Staffolani, Antunes**; Sbrascini, Leonardo; Bottoni, Luca; Minnetti, Luca; Darjazi, Hamideh; Trapananti, Angela; Paparoni, Francesco; Rezvani, S. Javad; Minicucci, Marco; Harfouche, Messaoud; Nobili, Francesco. Electrochemical characterization of γ-Fe_2O_3 and a reduced graphene oxide composite as a sustainable anode material for Na-ion batteries. *Energy Advances* Vol. 3 (2024), pp. 1726.

PATENTS

1) Patent (**granted**) “METODO PER LA RELITIAZIONE AD ELEVATA SOSTENIBILITA’ DELLA MATERIA ATTIVA DI UNA BATTERIA LFP ESAUSTA, NONCHE’ POLVERE RELITIATA CON TALE METODO E METODO PER LA REALIZZAZIONE DI UNA BATTERIA LFP A PARTIRE DALLA POLVERE RELITIATA”.
Inventors Dr. **Antunes Staffolani** (University of Camerino), Prof. Francesco Nobili (University of Camerino), Luca Minnetti (University of Camerino), Filippo girardi (Midac S.p.A.).

PROCEEDINGS

Oral communications

1) **Staffolani, Antunes.** "An Extensive Model for Solid Oxide Fuel Cells Based on Impedance Time-Based Deconvolution*". Bridging two centuries of electrochemical energy storage and conversion in honor of Prof. Roberto Marassi*, 4-5/02/2021, **Invited speaker.**
2) **Staffolani, Antunes**; Darjazi, Hamideh; Sbrascini, Leonardo; Bottoni, Luca; Tossici, Roberto; Nobili, Francesco. "Fast Charging Anode for LIBs and NIBs Based on Fe_3O_4/rGO: Synthesis and Characterization". *IWES 2021*, GISEL, 24-26/02/2021.
3) **Staffolani, Antunes;** Baldinelli, Arianna; Barelli, Linda; Bidini, Gianni; Nobili, Francesco. "Identification of Solid Oxide Cells Processes by Distribution of Relaxation Times: Model Creation and Validation". *SCI2021*, 14-23/09/2021,
4) **Staffolani, Antunes**, Nobili, Francesco; Sbrascini, Leonardo; Darjazi, Hamideh; Bottoni, Luca. "Synthesis and Characterization of Fe_3O_4/rGO as Anode Material for Na-ion Batteries". *XIII INSTM CONFERENCE*, 23-26/01/2022.
5) **Staffolani, Antunes;** Soavi, Francesca. "New Generation batteries: a sustainability approach". *NanoInnovation 2023*, Rome, 18-22/09/2023.
6) **Staffolani, Antunes**. "New Generation batteries: a sustainability approach". E-Tech 2024, Bologna, 07/05/2024. **Invited speaker.**
7) **Staffolani, Antunes**; Sbrascini, Leonardo; Minnetti, Luca; Nobili, Francesco; Finaurini, Edoardo. "Electrochemical Characterization of a Na-ion Cell based on Sn anode and Recycled $NaFePO_4$ cathode". 37th Topical Meeting of the International Society of Electrochemistry, 9-12/06/2024, Stresa, Italy.
8) **Staffolani, Antunes**; Trebbi, Andrea; Gregucci, Alessandro; Capodarca, Francesco; Soavi, Francesca. "Sustainable and Direct Recovery of Lithium-Ion Battery Cathodes using a Green Solvent". 75th ISE annual meeting, Montreal, Canada, 18-23/08/2024.
9) **Staffolani, Antunes**; Trebbi, Andrea; Ashir, Aishabibi; Mascetti, Federico; Giovannucci, Monica; Petri, Elisabetta; Samorì, Chiara; Rombolà, Alessandro G.; D'Agostino, Simone; Manyala, Ncholu; Soavi, Francesca. "Development of Sustainable Processes for LIBs Recycling" International Symposium on Beyond Li-Ion Batteries 2024 - BeLI24, Padova, 1-6/09/2024.

Poster presentations

10) **Staffolani, Antunes;** Carbonari, Gilberto; Maroni, Fabio; Darjazi, Hamideh; Nobili, Francesco. "Synthesis and Characterization of TiO_2@SnO_2 Nanocomposite as Viable Anode for Lithium-Ion Batteries". *Advanced Batteries for Automobile Applications 12*, Ulm, Germany, 6-9/10/2019.
11) **Staffolani, Antunes**; Darjazi, Hamideh; Tossici, Roberto; Nobili, Francesco. "Synthesis and characterization of high-performance and stability SnO_2/C composite anode for Li-ion batteries". *Advanced Batteries for Automobile Applications 12*, Ulm, Germany, 6-9/10/2019.

12) Baldinelli, Arianna; Barelli, Linda; Bidini, Gianni; Nobili, Francesco; **Staffolani, Antunes**. "Monitoring of Solid Oxide Fuel Cell Performance Through Deconvolution of Electrochemical Impedance Spectra". *Enerchem 2*, University of Padova, Italy, 12-14/02/2020.
13) **Staffolani, Antunes**; Baldinelli, Arianna, Bidini, Gianni; Nobili, Francesco; barelli, Linda. "Operando analysis of losses in commercial-size Solid Oxide Cells: Methodology development and validation". *GEI 2022*, Orvieto, 11-15/09/2022.
14) **Staffolani, Antunes**; Nobili, Francesco; Sbrascini, Leonardo; Darjazi, Hamideh; Bottoni, Luca; Minnetti, Luca. "Structural and Electrochemical Characterization of Iron oxide/rGO As Anode Material for Na-Ion Batteries". *ICNaB 2022*, Ulm, Germany, 06-08/12/2022.
15) **Staffolani, Antunes**; Trebbi, Andrea; Ashir, Aishabibi; Mascetti, Federico; Giovannucci, Monica; Petri, Elisabetta; Samorì, Chiara; Rombolà, Alessandro G.; Giorgetti, Marco; Manyala, Ncholu; Soavi, Francesca. "Designing Sustainable Processes for Lithium-ion Battery Recycling". 37th ISE Topical meeting, 9-12/06/2024.
16) Ashir, Aishabibi; **Staffolani, Antunes**; Trebbi, Andrea; Mascetti, Federico; Soavi, Francesca. "Design of Lithium-Ion Batteries Cathodes for Direct Recycling of Production Scraps". 75th ISE annual meeting, Montreal, Canada, 18-23/08/2024.

Abstracts

1) Synthesis and characterization of high-performance and stability SnO2/C composite anode for Li-ion batteries

Staffolani, Antunes; Darjazi, Hamideh; Tossici, Roberto; Nobili, Francesco.

Advanced Batteries for Automobile Applications 12, Ulm, Germany, 6-9/10/2019

In the recent years, the massive spreading of electric devices led the research to focus on high energy density technologies, especially Li-ion batteries[1]. Furthermore, with the increasing development of hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs), high-energy and high-power materials must be found[2].

In this regard, a composite anode based on SnO_2 and amorphous carbon have been prepared using commercial SnO_2 nanopowder and ACS sucrose as starting materials. SnO_2 nanoparticles were dispersed in ethanol solution of sucrose by ultrasonic wave, the solution was dried and the powder underwent thermal annealing at 600°C in Ar, giving the composite made of SnO_2:C in the approximate ratio 1:1. Structural characterization was pursued by XRD, SEM and TGA.

Electrodes have been prepared using high-molecular weight PAA as binder. Electrochemical characterization involved galvanostatic cycling, cyclic voltammetry, rate capability, GITT and PEIS; using $LiPF_6$ 1M in EC:DMC 1:1 + 2% VC electrolyte.

Cyclic voltammetries at different scan rates revealed a linear relationship between the peak current and the square root of scan rates, with an estimated lithium diffusion coefficient in accordance with literature[3,4]. Prolonged galvanostatic cycling shows improved stability and average specific capacity of 793 mAh g^{-1} at 500 mA g^{-1} with an efficiency close to 100 %. A specific capacity higher than 600 mAh g^{-1} was retained in rate capability test after current restoration to the initial state. PEIS applied every 10 cycles shows a remarkable stability of R_{SEI} and R_{ct} upon cycling.

Two main factors concur in determining this behaviour, namely: (i) the efficient dispersion of SnO_2 and carbon, which act as volume buffering matrix; (ii) improved conductivity thanks to amorphous carbon and (iii) the formation of a stabilized SEI by VC additive in the electrolyte.

2) Synthesis and Characterization of $TiO_2@SnO_2$ Nanocomposite as Viable Anode for Lithium-Ion Batteries

Staffolani, Antunes; Carbonari, Gilberto; Maroni, Fabio; Darjazi, Hamideh; Nobili, Francesco.

Advanced Batteries for Automobile Applications 12, Ulm, Germany, 6-9/10/2019

With the market growth and increasing development of hybrid electric vehicles (HEVs) and electric vehicles (EVs), high-energy density and high-power materials are needed. SnO2 is one of the proposed materials to replace the industry standard graphite (372 mAh g-1), thanks to its high theoretical capacity of 1411 mAh g-11; but its use is hindered by low cycling stability due to the volume expansion/contraction during alloying/dealloying reaction respectively.

In this regard, a composite anode material based on SnO2 and anatase TiO2 have been prepared using commercial SnO2 nanopowder and Ti-isopropoxide as starting materials. A sol-gel step, consisting in controlled hydrolysis of Ti-[O-iPr]4 in SnO2 dispersion followed by thermal annealing in inert atmosphere, yielded the composite made of SnO2:TiO2 in the approximate ratio 3:1. Structural characterization was pursued by XRD, SEM, TGA and Raman spectroscopy. Electrodes have been prepared using high-molecular weight PAA as binder, which is a greener alternative than PVdF and has better mechanical stability towards tin volume changes upon lithiation.

Cyclic voltammetries at different scan rates revealed a linear relationship between the peak current and the square root of scan rates, with an estimated lithium diffusion coefficient in accordance with literature2,3. Prolonged galvanostatic cycling shows improved stability and average specific capacity of 908 mAh g-1 at 1000 mA g-1 , together with remarkable rate capability. PEIS applied every 10 cycles revealed a stable SEI upon cycling. Two main factors concur in determining this behaviour, namely: (i) the efficient dispersion of SnO2 and TiO2, which act as volume buffering matrix; (ii) the formation of a stabilized SEI by VC additive in the electrolyte.

3) Monitoring of Solid Oxide Fuel Cell Performance Through Deconvolution of Electrochemical Impedance Spectra

Baldinelli, Arianna; Barelli, Linda; Bidini, Gianni; Nobili, Francesco; **Staffolani, Antunes**.

Enerchem 2, University of Padova, Italy, 12-14/02/2020.

In this study we present a method to identify the main processes behind polarization losses in Solid oxide cells (SOCs), in order to build an equivalent circuit model (ECM) suitable for real-time diagnosis based on EIS measurement.

SOCs are one of the most efficient energy conversion system, yet a performance drop may be caused by either unfavourable operating conditions or derating factors. Therefore, in-operando analysis techniques are useful to characterize material fitness and to detect early stages of degradation[1].

Electrochemical impedance spectroscopy (EIS) and its distribution of relaxation times (DRT) is a powerful and non-destructive tool to address the physio-chemical processes occurring inside the cell, as well as modification in the membrane electrode assembly[2]. In order to find the proper ECM, we have performed a wide experimental campaign on a commercial SOC by changing several working parameters such as: temperature (640-820°C), current density (0-1500 mA cm^{-2}), fuel flow (150 ± 50 mL min^{-1}) and its composition (H_2 from 100%$_{vol}$ to 50%$_{vol}$ and 25%$_{vol}$ on dry basis, balanced with N_2).

As relaxation time lengthens, DRT deconvolution highlights five major processes, namely: reaction and charge transfer at the triple phase boundary, anodic diffusion, charge transfer at the cathode and cathodic diffusion.

4) Fast Charging Anode for LIBs and NIBs Based on Fe_3O_4/rGO: Synthesis and Characterization

Staffolani, Antunes; Darjazi, Hamideh; Sbrascini, Leonardo; Bottoni, Luca; Tossici, Roberto; Nobili, Francesco.

IWES 2021, GISEL, 24-26/02/2021

In this study we present the synthesis and characterization of a Fe_3O_4-based nanocomposite anode for LIBs and NIBs.

Several transition metal oxides have been studied for both mentioned alkali-ion batteries because of their high specific capacity such as Co_3O_4 (890 mAh g^{-1}), SnO_2 (1494 mAh g^{-1}) and Fe_3O_4 (924 mAh g^{-1})[1,2]. The latter is certainly a good candidate thanks to its low toxicity, low cost and earth abundancy.

Anyway, several issues must be faced to make it suitable for real application e.g., the remarkable structural change and volume expansion which can lead to the electrode pulverization and eventually capacity decay[3].

Herein we report a facile one-pot synthesis of Fe_3O_4 nanoparticles (**Fe_3O_4 nps**) by a base-promoted coprecipitation, and a facile and quick embedding of Fe_3O_4 nanoparticles into reduced graphene oxide (**Fe_3O_4/rGO**), given by a sonochemical approach and chemical reduction. The obtained materials are structurally characterized by XRD, SEM and Raman spectroscopy. The electrochemical behaviour is studied by CV, galvanostatic cycling, rate capability and PEIS.

Thanks to this rapid and simple approach, the Fe_3O_4 nps and rGO are linked together without the need of any other molecular linkers, leading to remarkable properties such as a specific capacity of ≈ 980 mAh g^{-1} at 4C (3.7 A g^{-1}) in LIBs and ≈ 300 mAh g^{-1} at 1 A g^{-1} in NIBs.

5) Identification of Solid Oxide Cells Processes by Distribution of Relaxation Times: Model Creation and Validation

Staffolani, Antunes; Baldinelli, Arianna; Barelli, Linda; Bidini, Gianni; Nobili, Francesco.
SCI2021, 14-23/09/2021

Solid oxide cells (SOCs) represent one of the most efficient and promising electrochemical technologies for hydrogen energy conversion[1]. Understanding and monitoring degradation is essential for their full development and wide diffusion. Advanced processing of experimental data, such as Distribution of Relaxation Times (DRT) on Electrochemical Impedance Spectroscopy (EIS) measurements, is a powerful tool to investigate physicochemical processes occurring in SOCs and to analyses ageing mechanisms[2]. In the first part, a method is presented to identify the processes behind the polarization losses in order to build a proper equivalent circuit model (ECM) suitable for the operando diagnosis based on EIS. In the second part, a validation of the electrochemical model is done, by applying an a priori known stress agent to a SOC operated in laboratory conditions and analyzing the deconvolution of electrochemical impedance spectra. Finally, experimental evidence obtained from a fully operando approach was counterchecked through ex-post material characterization.

6) Synthesis and Characterization of Fe_3O_4/rGO as Anode Material for Na-ion Batteries

Staffolani, Antunes, Nobili, Francesco; Sbrascini, Leonardo; Darjazi, Hamideh; Bottoni, Luca.
XIII INSTM CONFERENCE, 23-26/01/2022

Introduction

Iron oxide-base anodes are certainly good candidate anode materials for NIBs thanks to their low toxicity, low cost and earth abundancy. However, several issues must be faced to make them suitable for real application e.g., the remarkable structural change and volume expansion which can lead to the electrode pulverization and eventually capacity decay.

Material and Methods

PAA (m.w. 450000 g/mol), $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, PC, DMC, $NaClO_4$, N_2H_4, NH_4OH, EC Graphene oxide (C:O ratio of 5:4.3) were used as received. Fe_3O_4 nanoparticles have been synthesized by a coprecipitation method. The composite Fe_3O_4/rGO have been synthesized by embedding Fe_3O_4 nanoparticles into GO via a sonochemical route. Structural and morphological characterization involved SEM, XRD, and Raman scattering. Electrochemical characterization involved GCPL, CV, rate capability, PEIS, and Ex-situ Raman scattering.

Results

Structural and morphological characterization highlights Fe_3O_4 nanoparticles having a dimension of ≈ 5nm, and their effective embedding into the carbonaceous matrix. Electrochemical characterization revealed a high specific capacity of 300 mAh g^{-1} at I = 1000 mA g^{-1}, retained to 113 mAh g^{-1} at I = 5 A g^{-1}. CV at different scan rates proved a linear relationship between I and $v^{1/2}$ and a b-value between 0.5 < b < 1. A further interface modelled by an RQ parallel have been found with PEIS. The A_{1g} peak of Fe_3O_4 reversibly changes according to the sodiation degree.

Discussion

The small Fe_3O_4 particles size coupled to the electronic conductivity and mechanical resistance of rGO reflect in a high stability upon cycling as well as a high-rate capability. A redox-pseoudcapacitive behavior i.e., near-surface adsorption of ionic species concurrent with a faradaic process was proved by CV at different scan rates. The extra interphase layer found by PEIS could be a large Na_2O layer which acts as a transport barrier, thus limiting the specific capacity. As demonstrated by Ex-situ Raman scattering, the conversion reaction is reversible and a small quantity of Fe_3O_4 did not participate to the charge-storage reaction.

7) Operando analysis of losses in commercial-size Solid Oxide Cells: Methodology development and validation

Staffolani, Antunes; Baldinelli, Arianna, Bidini, Gianni; Nobili, Francesco; barelli, Linda.

GEI 2022, Orvieto, 11-15/09/2022

The clean energy transition boasts new efficient and decarbonised energy conversion and storage solutions [1]. In this roadmap, hydrogen and fuel cells are considered game-changing technologies [2]. In this context, Solid Oxide Cells (SOCs) deserve attention for their capability of reverse operation, both as power generators (SOFC, fuel cell operation mode) and power-to-gas technology (SOE, electrolyser operation mode) [3]. Lifetime is a crucial indicator to grant the technology's success and boost the commercial stage of development. It is necessary to fully understand the impact of the real operation on SOCs materials. To this end, this work firstly focuses onto identifying the physico-chemical phenomena behind performance losses via electrochemical impedance spectroscopy (EIS) and distribution of relaxation times (DRT). A systematic approach has been used to isolate each physico-chemical phenomena by acquiring impedance spectra at different working temperature (640-820 °C), O_2 % in the air electrode (5-25 $\%_{vol}$), as well as H_2 (7-97$\%_{vol}$) and water steam (3-50$\%_{vol}$) in the fuel electrode. According to the experimental evidence collected, the main contributions to the cell impedance are identified as charge transfer (DRT peak at 10^4 Hz), oxygen diffusion (DRT peak at 10^3 Hz) and gas diffusion in the fuel electrode (double DRT signal in the frequency range 1-100 Hz). The results are validated with the ECM methodology, implementing a $LR_{el}(R_{ct}Q)GW_{FLW}$ circuit shown in Figure 1.

8) Structural and Electrochemical Characterization of Iron oxide/rGO As Anode Material for Na-Ion Batteries

Staffolani, Antunes; Nobili, Francesco; Sbrascini, Leonardo; Darjazi, Hamideh; Bottoni, Luca; Minnetti, Luca.

ICNaB 2022, Ulm, Germany, 06-08/12/2022

Iron oxide-base anodes are certainly good candidate anode materials for NIBs thanks to their low toxicity, low cost and earth abundancy[1,2]. However, several issues must be faced to make them suitable for real application e.g., the remarkable structural change and volume expansion which can lead to the electrode pulverization and eventually capacity decay.

Iron oxide nanoparticles have been synthesized by a coprecipitation method. The composite iron oxide/rGO have been synthesized by embedding iron oxide nanoparticles into GO via a sonochemical route. Structural and morphological characterization involved SEM, XRD, and Raman scattering. Electrochemical characterization involved GCPL, CV, rate capability, PEIS, and Ex-situ Raman scattering.

The small particles size of the active material coupled to the electronic conductivity and mechanical resistance of rGO reflect in a high stability upon cycling as well as a high-rate capability (300 mAh g^{-1} at I = 1000 mA g^{-1}, retained to 113 mAh g^{-1} at I = 5 A g^{-1}). Ex-situ Raman scattering shows that the conversion reaction is reversible and a small quantity of iron oxide did not participate to the charge-storage reaction.

9) New Generation batteries: a sustainability approach

Staffolani, Antunes; Soavi, Francesca.

NanoInnovation 2023, Rome, 18-22/09/2023

Li-ion batteries are currently dominating the market of energy storage devices and have been appointed as the main energy storage system for transport electrification and renewable energy sources. In the next decade, this will result with a serious waste-management issue of End-of-Life batteries. To achieve a sustainable mobility and ensure the economical circularity of LIBs in the future, this issue must be addressed. Nevertheless, these events can be an opportunity for battery manufacturers, recyclers, and the European Union. On one hand, battery recycling is a profitable market thanks to the valuable metals inside of it; on the other hand, it is also a chance for the European Union to reduce its dependence on foreign countries for the supply of battery raw materials. These recycling procedures should simultaneously address sustainability, recovery efficiency of Critical Raw Materials (CRMs), and re-use of solvents following the Green Chemistry principles[1,2]. In this seminar, the PNRR action of the Enercube lab of University of Bologna as well as other ongoing projects targeting the LIBs recycling and design for recycling will be presented and discussed[3,4,5].

10) New Generation batteries: a sustainability approach

Staffolani, Antunes.

E-Tech 2024, Bologna, 7-8/05/2024

Li-ion batteries have been appointed as the main energy storage system for transport electrification and renewable energy sources. Energy and power density are the key figures of merit for most electrochemical energy storage systems. Especially for automotive applications, electrochemical devices able to withstand fast-charging conditions and high-power are needed. The power capability of such devices is strictly dependent on the used materials and their reaction kinetics. In this seminar, the PNRR action of the Enercube lab of University of Bologna as well as other ongoing projects targeting LIBs and other electrochemical power sources such as supercapacitors.

11) Electrochemical Characterization of a Na-ion Cell based on Sn anode and Recycled $NaFePO_4$ cathode

Staffolani, Antunes; Sbrascini, Leonardo; Minnetti, Luca; Nobili, Francesco; Finaurini, Edoardo.

37th ISE topical meeting, Stresa, 9-12/06/2024

Thanks to their excellent characteristics, Li-ion batteries have revolutionized the battery and energy storage market[1]. Indeed, they are the energy storage system of choice when talking about portable electronics (smartphones, laptops, etc.) and electrified vehicles (xEV). However, LIBs will not be able to satisfy the prospected energy demand due to the scarcity and heterogeneous presence of its raw materials [1,2].
Therefore, in the last decade the research efforts have been focused on alternative electrochemical energy storage devices such as Na-ion batteries [3–5].
In this work, an in-depth analysis of a Na-ion battery based on alloying-type anode and an olivine cathode is presented. In half-cell, the anode, based on Sn, shows outstanding electrochemical performances, with a specific capacity of ≈ 700 mAh g^{-1} (areal capacity of ≈ 2.5 – 3 mAh cm^{-2}) and an excellent capacity retention of 98 % after 500 cycles. The studied cathode is $NaFePO_4$ obtained via recycling of $LiFePO_4$ from spent LFP-based batteries. LFP, once extracted from the positive electrodes, underwent a chemical de-lithiation process, and, at a later stage, a chemical sodiation.
For both materials (anode and cathode), the synthesis and characterization methods are described in detail, from a structural, morphological, and electrochemical point of view. Both electrodes have been optimized in terms of thickness, loading of active materials, electrode density. Eventually, the full electrochemical characterization of a Sn|1M $NaPF_6$|$NaFePO_4$ cell is shown.

12) Designing Sustainable Processes for Lithium-ion Battery Recycling

Staffolani, Antunes; Trebbi, Andrea; Ashir, Aishabibi; Mascetti, Federico; Giovannucci, Monica; Petri, Elisabetta; Samorì, Chiara; Rombolà, Alessandro G.; Giorgetti, Marco; Manyala, Ncholu; Soavi, Francesca.

Strategies that simultaneously target energy performance, sustainable manufacturing processes, valorization of green raw materials, and easy recycling of lithium-ion batteries (LIBs) are urgently needed. Three are the main approaches to manage End-of-Life (EoL) LIBs: Remanufacturing, repurposing and recycling [1]. Recycling is the best option since exhausted LIBs are considered a huge reserve of secondary raw materials to produce new LIBs, within a circular economy approach [1]. Each recycling strategy is specifically designed and selected according to cell design (prismatic, pouch, coin cell), electrode chemistry, and state of charge. Thus, a strategy for sorting the different batteries is mandatory for an efficient recycling process [2]. Furthermore, an efficient and safe disassembly route is needed to avoid any potential risks. The polymer binder needs to be removed to collect the electrode active materials. Organic solvents with great affinity to the binder like NMP, DMAC, DMF, and DMSO are generally used for this purpose. However, waste solutions from this process pose environmental hazards that need to be treated; therefore, the use of green solutions is mandatory. Citrus fruit juice and, recently, cyrene, and triethylphosphate were proposed for a green solvent-based separation process [3,4]. An alternative route is to design the electrode manufacturing with water-soluble binders, which not only decreases the production cost of LIBs electrode, but also improve their recyclability. Eventually, the electrode active materials can be either directly recycled or recycled by a hydrometallurgical approach. In the latter, leaching is the key step to convert the metals of cathode active materials into ions in a solution. Deep eutectic solvents are an emerging solution for the leaching of battery materials [5], which can then be used for the recovery of valuable metals or to build new devices such as hybrid supercapacitors.

Herein, we give an overview of the research activities carried out at the Enercube lab of University of Bologna about the design of sustainable processes for LIBs recycling and design easier to recycle batteries.

13) Sustainable and Direct Recovery of Lithium-Ion Battery Cathodes using a Green Solvent

Staffolani, Antunes; Trebbi, Andrea; Gregucci, Alessandro; Capodarca, Francesco; Soavi, Francesca.

75th ISE annual meeting, Montreal, Canada, 18-23/08/2024.

Lithium-ion batteries (LIB) continue to dominate the energy storage landscape. Widely utilized in portable electronic devices, electric vehicles, and renewable energy systems, LIB offer high energy density, longer cycle life, and relatively low self-discharge rates. Ongoing research and development efforts focus on enhancing performance, increasing energy density, and addressing concerns related to cost and environmental impact. Indeed, as the demand and use continues to arise, the need for effective recycling methods becomes increasingly important.

Recycling of spent LIBs close the loop of electrodes materials due to the direct use of spent active material as secondary raw materials to produce fresh electrodes. For direct recycling processes, the active materials must be detached from their respective current collectors [1]. Commonly, this is achieved by the thermal decomposition of the polyvinylidene difluoride (PVdF) binder at ≈ 400/500 °C [2], leading to the formation of HF and organofluorine compounds, or with dipolar aprotic solvents such as N-methyl pyrrolidone (NMP), N,N-dimethyl formamide (DMF), and N,N-dimethyl acetamide (DMAC). However, such solvents present epatoxicity, skin irritation effects, and are toxic for the reproductive system (H312, H319, H332, H360); thus, they cannot be used in large scale processes. Recently, other greener options have been investigated in literature [3,4].

This study aims to directly recover the cathode active material as well as the polymeric binder for a second production of new cathodes. The detachment from the aluminum current collector was done using a green solvent (triethylphosphate) and optimized by investigating different dissolution times, working temperatures and solid to liquid ratios. After that, the recovered active material as well as the binder were characterized by different techniques, such as X-Ray Diffraction (XRD), Infrared spectroscopy (IR), thermogravimetric analysis (TGA), and Differential Scanning Calorimetry (DSC). Lastly, the active material and the binder were electrochemically tested and compared to the pristine ones using Galvanostatic Cycling with Potential Limitation (GCPL) and Cycling Voltammetry (CV). This work could open new routes and strategies for direct recovery as well as gain interest for manufacturing companies.

14) Design of Lithium-Ion Batteries Cathodes for Direct Recycling of Production Scraps

Ashir, Aishabibi; **Staffolani, Antunes**; Trebbi, Andrea; Mascetti, Federico; Soavi, Francesca.

75th ISE annual meeting, Montreal, Canada, 18-23/08/2024.

Lithium-ion batteries (LIBs) debuted in 1991 and have since become a primary energy source for portable electronic devices like mobile phones and laptops. Currently, LIBs are expanding their application scope to include large-scale power solutions and energy storage systems, as evident in their integration into electric vehicles and renewable energy infrastructures. This diversification is driven by the quest for higher energy density and comparable power density, surpassing that of alkaline batteries. As the demand for and utilization of LIBs continue to rise, the imperative for efficient recycling methods becomes increasingly crucial.

The recycling of spent LIBs involves utilizing spent active materials as secondary raw materials for new electrode production, completing the electrode material cycle. In addition, the worldwide increase of battery cell manufacturing rate calls for an efficient recovery of electrode scraps. Direct recovering and re-use of electrode scrap material can have a great impact in decreasing both environmental and economic impact of cell manufacturing.

To enhance this direct recycling process, novel cathode designs are essential. The prevalent F-based binder, poly(vinylidene difluoride) (PVDF), provides chemical and electrochemical stability but poses environmental challenges both in the production and recycling phases. Indeed, PVDF beside being a fluoruated compound, is mainly soluble in the toxic solvent N-methyl-2-pyrrolidone (NMP). Its use in electrode processing requires costly controlled environments, affecting both economic and environmental aspects of LIB manufacturing. The drying and NMP recovery process incurs a substantial energy demand, raising environmental concerns with fluorocarbon generation during incineration. To address these challenges and promote sustainability, extensive efforts are underway to replace PVDF with F-free and water-soluble polymers.

This research focuses on designing $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) LIB cathodes in view of their greener manufacturing and recovery from production scraps. We explored the use of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), a conductive and porous polymer known for its electrical, mechanical, self-healing, and high biocompatibility properties. Additionally, pullulan, a natural and inert polymer with recent applications in energy storage systems, was studied as binder component in PEDOT:PSS blends. To aid easier separation of cathode active materials during direct recycling process, graphite flakes were used for production of LMNO electrode. The evaluation of cell performance included the analysis of voltammetric and galvanostatic charge/discharge cycles at different C-rates. This assessment utilized a 1M $LiPF_6$ electrolyte in a 1:1 (v:v) blend of ethylene carbonate (EC) and dimethyl carbonate (DMC) referred to as LP30. Subsequently, the results were compared with the performance of cells fabricated using LMNO and PVDF.

15) Development of Sustainable Processes for LIBs Recycling

Staffolani, Antunes; Trebbi, Andrea; Ashir, Aishabibi; Mascetti, Federico; Giovannucci, Monica; Petri, Elisabetta; Samorì, Chiara; Rombolà, Alessandro G.; D'Agostino, Simone; Manyala, Ncholu; Soavi, Francesca.

International Symposium on Beyond Li-Ion Batteries 2024 - BeLI24, Padova, 1-6/09/2024.

Li-ion batteries are currently dominating the market of energy storage devices and have been appointed as the main energy storage system for transport electrification and renewable energy sources. In the next decade, this will result with a serious waste-management issue of End-of-Life batteries. To achieve a sustainable mobility and ensure the economical circularity of LIBs in the future, this issue must be addressed. Nevertheless, these events can be an opportunity for battery manufacturers, recyclers, and the European Union. On one hand, battery recycling is a profitable market thanks to the valuable metals inside of it; on the other hand, it is also a chance for the European Union to reduce its dependence on foreign countries for the supply of battery raw materials [1]. Each recycling strategy is specifically designed and selected according to cell design (prismatic, pouch, coin cell), electrode chemistry, and state of charge [2]. The polymer binder needs to be removed to collect the electrode active materials. Organic solvents with great affinity to the binder like NMP, DMAC, DMF, and DMSO are generally used for this purpose. However, waste solutions from this process pose environmental hazards that need to be treated [1]; therefore, the use of green solutions is mandatory. Citrus fruit juice and, recently, Cyrene®, and triethylphosphate were proposed for a green solvent-based separation process [3,4]. Eventually, the electrode active materials can be either directly recycled or recycled by a hydrometallurgical approach. In the latter, leaching is the key step to convert the metals of cathode active materials into ions in a solution. Deep eutectic solvents are an emerging solution for the leaching of battery materials [5], which can then be used for the recovery of valuable metals or to build new devices such as hybrid supercapacitors. Herein, we give an overview of the research activities carried out at the EnerCUBE lab of University of Bologna about the design of sustainable processes for LIBs recycling and design easier to recycle batteries.